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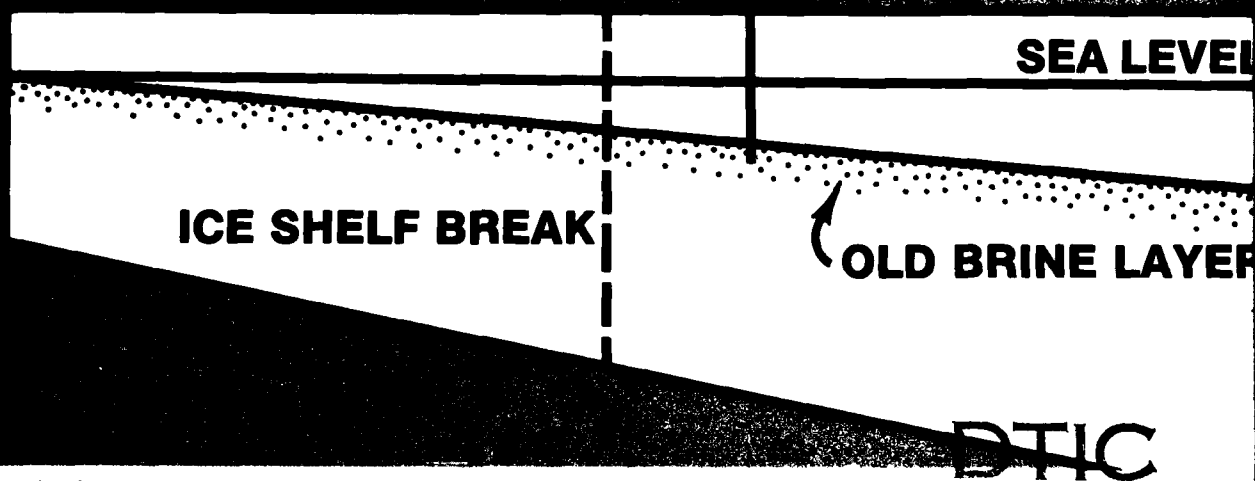
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Chemical fractionation of brine in the McMurdo Ice Shelf, Antarctica

SEA LEVEL

ICE SHELF BREAK

OLD BRINE LAYER

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Chemical fractionation of brine in the McMurdo Ice Shelf, Antarctica

J.H. Cragin, A.J. Gow and A. Kovacs

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During the austral summers of 1976–77 and 1978–79, several ice cores were taken from the McMurdo Ice Shelf brine zone to investigate its thermal, physical and chemical properties. This brine zone consists of a series of superimposed brine layers (waves) that originate at the seaward edge of the ice shelf and migrate at various rates, depending upon their age and position in the ice shelf. The brine in these layers becomes increasingly concentrated as the waves migrate inland through the permeable ice shelf firn. Chemical analyses of brine samples from the youngest (uppermost) brine wave show that it contains sea salts in normal seawater proportions. Further inland, deeper and older brine layers, though highly saline ($S > 200$ ‰ percent), are severely depleted in SO_4^{2-}, with the SO_4^{2-}/Na^+ ratio being an order

20. Abstract (cont'd).

of magnitude less than that of normal seawater. Analyses of Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-} and Cl^-, together with solubility and temperature considerations, show that the sulfate depletion is due to selective precipitation of mirabilite, $Na_2SO_4 \cdot 10H_2O$. The location of the inland boundary of brine penetration is closely related to the depth at which the brine encounters the firn/ice transition. However, a small but measurable migration of brine is still occurring in otherwise impermeable ice; this is attributed to eutectic dissolution of the ice by concentrated brine as it moves into deeper and warmer parts of the McMurdo Ice Shelf.

PREFACE

CHEMICAL FRACTIONATION OF BRINE IN THE MCMURDO ICE SHELF, ANTARCTICA

J.H. Cragin, A.J. Gow and A. Kovacs

INTRODUCTION

Seawater infiltration into porous ice shelves has been observed at a number of Antarctic locations (Dubrovin 1962, Yevteyev 1962, Stuart and Bull 1963, Heine 1968, Thomas 1975, Kovacs and Gow 1975, 1977, Kovacs et al. 1982a). Much of the past work has focused on either determining the geographical extent of the brine penetration inland using radio echo sounding techniques (Clough 1973, Kovacs and Gow 1975) or on studying ice shelf–brine thermodynamics (Thomas 1975). Initially, brine layer formation was believed to be due to vertical infiltration of seawater into porous firn (Stuart and Bull 1963) but Risk and Hochstein (1967) and Kovacs and Gow (1975) have concluded from their observations on the McMurdo Ice Shelf that lateral infiltration of seawater from the shelf edge is the dominant mechanism of brine infiltration. More recent observations by Kovacs et al. (1982b) show that lateral infiltration is itself dominated by wave-like intrusions of seawater triggered by periodic break-out (calving) of the ice front in McMurdo Sound.

In order for brine to remain liquid at the temperatures encountered in ice shelves, excess water must be eliminated by freezing within the pores of the permeable firn. Freeze concentration could also lead to significant changes in brine chemistry. The only reported chemical measurements of the composition of the infiltrated brine are those of Wilson and Heine (1964) and Heine (1968) who observed a SO_4* depletion relative to Cl in the brine layer of the McMurdo Ice Shelf. They attributed this to preferential precipitation of mirabilite, $Na_2SO_4 \cdot 10H_2O$, which begins to take place at a temperature of $-8.2\,°C$ (Assur 1958). Here we report results of more extensive chemical analyses of a series of ice cores taken from the top of the brine layer in the McMurdo Ice Shelf.

EXPERIMENTAL PROCEDURES

Core drilling and sampling

An electromechanical drill designed by Rand (1976) was used to obtain 10-cm-diameter cores from the snow surface down to about 3 m into the brine layer. In this particular drill the electrical section leading to the motor was not designed to operate in liquids, so it was not possible to drill deeper than about 3 m into the brine layer. We obtained additional cores with a modified SIPRE coring auger. Cores were drilled at the locations shown in Figure 1. The cores labeled 77 High Step and 77 Low Step were drilled during January 1977; cores from locations A, B, C, D and E were drilled during November 1978.

Sections of brine-soaked firn and ice were cut from cores at about 10-cm intervals, melted in

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* For brevity and ease of typesetting, ionic charges have been omitted from the elemental symbols. It should be noted, however, that measurements and ratios reported are those for the respective ions.
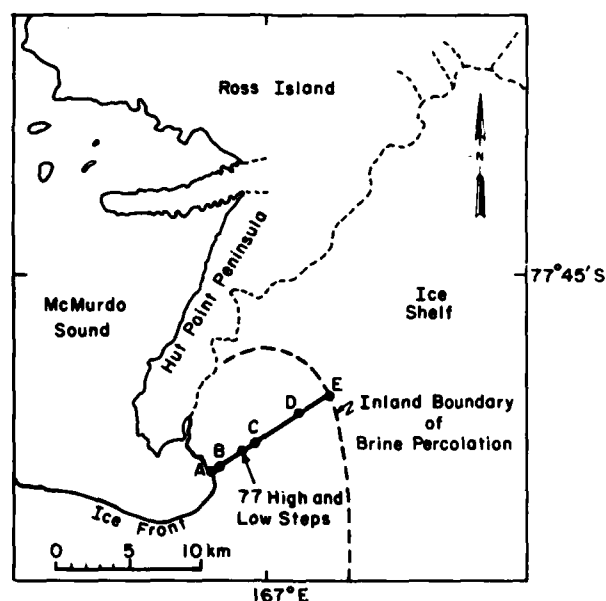
Figure 1. Sketch map of McMurdo Ice Shelf area showing main profile line and core drilling locations.

polyethylene containers and transferred to glass vials for shipment to CRREL for chemical analysis.

Cation analyses

We performed cation analyses for Na, K, Ca and Mg on the melted samples, which had been diluted by factors of 10^4 to 10^6, depending upon the element and the sample salinity. Concentrations were determined on 20-μL aliquots by graphite furnace atomic absorption using a Perkin–Elmer Model 403 AA spectrophotometer in conjunction with a Model 2200 Heated Graphite Atomizer. Deuterium background correction was unnecessary at the low concentrations (μg/L) of the diluted samples. Analysis for Na, however, did require a maximum temperature (approximately 2700 °C) heating step after each atomization to remove residual salts and prevent interference in the signal of subsequent aliquots. Standards, prepared fresh daily from Fisher 1000-mg/L stock solutions, and samples were analyzed in triplicate.

Sulfate and chloride analyses

Sulfate concentrations were determined turbidimetrically using $BaCl_2$ with a stabilizing agent to form $BaSO_4$ suspension. Samples were diluted by factors of 2 to 100 to bring their SO_4 concentrations into the analytical working range of 5 to 50 mg/L. Absorbances were measured in 2.5-cm cells at 450 nm with a Hach DR/2 spectrometer.

Table 1. Comparison of sulfate determined by turbidimetric (barium sulfate) and colorimetric (barium chloranilate) techniques.

Samples are from the 77 High and 77 Low Step cores.

| | SO_4 concentration (g/L) | |
Sample	Turbidimetric	Colorimetric
1A	3.4 ± 0.1*	3.8
2	2.4 ± 0.1	2.5 ± 0.1
5A	2.2 ± 0.1	2.3 ± 0.1
5B	2.4 ± 0.1	2.5 ± 0.1
33C	0.55 ± 0.03	0.57 ± 0.02
34B	0.60 ± 0.02	0.60 ± 0.01

* Standard deviations shown are for triplicate analyses. For the colorimetric analysis of sample 1A, sufficient sample was available for only a single analysis.

As a check on the above turbidimetric method, we also analyzed selected samples for SO_4 using the more involved barium chloranilate technique (Bertolacini and Barney 1958, Shafer 1967) modified as previously described (Cragin et al. 1975) without sample preconcentration. A comparison (Table 1) of results of these two methods shows excellent agreement.

Chloride concentrations were determined potentiometrically using an Orion solid-state Cl electrode and an Orion double junction reference electrode with 1 M KNO_3 filling solution in the outer

Table 2. Sample depths, meltwater salinities, chemical concentrations and SO₄/Na ratios for all brine-infiltrated ice core samples from McMurdo Ice Shelf, Antarctica.

Drill hole	Sample	Depth (m)	S (°/₀₀)	Na (g/L)	SO₄ (g/L)	SO₄/Na
A	1-1	2.60–2.70	4.2	1.3	0.28	0.22
	1-2	3.10–3.20	5.7	1.9	0.43	0.23
	1-3	4.00–4.10	3.0	1.1	0.19	0.17
	1-4	4.70–4.80	3.3	1.2	0.24	0.20
	1-5	8.30–8.40	3.2	1.5	0.24	0.16
B	4-B	8.95–9.05	6.9	2.2	0.65	0.29
	4-C	9.05–9.15	8.2	2.6	0.73	0.28
	4-D	9.15–9.25	7.4	2.4	0.68	0.28
	4-E	9.25–9.35	7.2	2.4	0.65	0.27
	4-F	9.35–9.45	4.9	1.8	0.40	0.22
	4-G	9.45–9.55	2.9	1.2	0.24	0.20
	4-H	9.55–9.65	3.7	1.4	0.31	0.22
	4-J	9.75–9.85	2.2	1.1	0.23	0.21
	4-K	9.85–9.95	3.0	0.95	0.20	0.21
	4-L	9.95–10.05	3.0	1.15	0.25	0.22
	4-M	10.05–10.15	2.5	1.15	0.26	0.23
	4-N	10.15–10.25	3.1	1.1	0.22	0.20
	4-O	10.25–10.35	3.1	1.1	0.23	0.21
	4-P	10.35–10.45	—	1.0	0.21	0.21
77 High Step	1-A	17.05–17.25	15.2	5.0	3.8	0.68
	1-B	17.25–17.40	13.0	4.0	2.2	0.55
	2	17.54–17.64	12.2	3.7	2.5	0.65
	3	17.72–17.92	16.0	4.4	2.6	0.59
	4-A	17.95–18.05	14.0	4.2	2.1	0.50
	4-C	18.15–18.27	15.5	5.4	—	—
	5-A	18.30–18.40	16.0	3.9	2.3	0.56
	5-B	18.45–18.55	12.6	4.1	2.5	0.59
	5-D	18.70–18.76	13.0	3.9	2.4	0.62
77 Low Step	33-B	22.05–22.15	15.0	3.5	0.32	0.091
	33-C	22.15–22.20	25.5	6.4	0.68	0.110
	33-D	22.20–22.25	30.0	8.7	0.57	0.063
	34-B	22.31–22.41	30.0	11.0	0.60	0.055
C (78 High Step)	C-2	19.55–19.69	14.0	4.7	1.25	0.27
	C-3	19.69–19.95	8.9	3.2	0.95	0.30
	Z-1	19.95–20.10	13.5	4.7	1.45	0.31
	Z-2	20.10–20.20	15.3	5.3	2.1	0.40
	Z-3	20.20–20.30	—	3.1	0.95	0.31
	Z-4	20.30–20.40	10.5	3.8	1.4	0.37
	Z-5	20.40–20.50	11.0	3.6	1.1	0.31
	Z-7	20.80–20.95	8.1	3.1	0.75	0.24
D	B-1	33.70–33.84	0.4	0.10	<0.01	<0.10
	B-2	33.84–34.00	0.4	0.08	0.004	0.049
	B-3	34.00–34.16	1.8	0.45	0.014	0.031
	B-4	34.16–34.36	4.4	1.3	0.034	0.026
	B-5	34.39–34.54	5.3	1.5	0.042	0.028
	B-6	34.54–34.69	13.1	3.5	0.100	0.029
	B-7	34.69–34.84	14.6	3.8	0.110	0.029
	B-8	34.84–34.99	8.1	2.8	0.080	0.029
	B-9	34.99–35.22	10.8	3.6	0.090	0.025
	B-T	35.22–35.32	13.4	4.1	0.115	0.027
	B-M	35.94–36.04	9.5	2.6	0.090	0.035
	B-B	36.57–36.67	11.0	3.2	0.085	0.028

Table 2 (cont'd). Sample depths, meltwater salinities, chemical concentrations and SO$_4$/Na ratios for all brine-infiltrated ice core samples from McMurdo Ice Shelf, Antarctica.

Drill hole	Sample	Depth (m)	S (⁰/₀₀)	Na (g/L)	SO$_4$ (g/L)	SO$_4$/Na
E	A-C	50.47–50.57	2.0	0.60	0.018	0.030
	A-D	50.57–50.67	1.3	0.39	0.012	0.031
	A-E	50.67–50.77	3.0	0.81	0.026	0.032
	A-F	50.77–50.87	2.2	0.67	0.020	0.030
	A-G	50.87–50.97	1.0	0.34	0.010	0.029
	A-I	51.07–51.17	10.1	3.8	0.120	0.032
	B-A	51.17–51.29	7.0	3.2	0.075	0.023
	B-B	51.29–51.39	9.2	2.8	0.080	0.029
	B-C	51.39–51.50	2.7	0.87	0.026	0.030
	B-D	51.50–51.60	2.2	0.57	0.015	0.026
	B-E	51.60–51.70	15.0	4.0	0.080	0.020
	B-F	51.70–51.81	4.1	1.8	0.036	0.020
	B-G	51.81–51.94	1.4	0.32	0.008	0.025
	B-H	51.94–52.07	9.6	2.1	0.065	0.031
	C-A	52.07–52.16	14.6	5.0	0.13	0.026
	C-B	52.16–52.25	0.2	0.10	≈0.002	0.020
	C-C	52.25–52.34	2.1	0.70	0.020	0.029
	C-E	52.43–52.52	3.2	0.98	0.028	0.029
	Free brine	Bottom of hole	~200	62	2.1	0.034
Copenhagen Standard Seawater, observed				10.4	2.76	0.27
Copenhagen Standard Seawater, expected*			34.5	11.0	2.79	0.25

* From Riley and Chester (1971).

Table 3. Concentrations of K, Ca, Mg and Cl in selected brine samples, and corresponding ionic ratios.

Drill hole	Sample	K (g/L)	Ca (g/L)	Mg (g/L)	Cl (g/L)	Na/K	Na/Ca	Na/Mg	Cl/Na
B	4-K				1.2				1.3
	4-M		0.29	0.13			40	8.8	
77 High Step	1-A	0.15	0.18	0.58		33	28	8.6	
	1-B				6.7				1.7
	2	0.10	0.18	0.47		37	21	7.9	
	4-A	0.13					32		
	5-A	0.13	0.20	0.62	9.0	30	20	6.3	2.3
	5-B		0.16	0.52			27	7.9	
77 Low Step	33-B		0.19	0.58			19	6.6	
	33-C	0.27				24			
	33-D	0.29	0.31	1.15		30	28	7.6	
	34-B	0.37	0.36	1.29		30	31	8.5	
C	C-2		0.155	0.55	8.2		30	8.6	1.7
	Z-1				7.0				1.5
	Z-2				10.0				1.9
	Z-4				5.4				1.4
	Z-5				6.0				1.7
D	B-4				2.7				2.1
	B-5				2.9				1.9
	B-T				5.3				2.0
A	B-E		0.13	0.41			31	9.8	
	B-G		0.010	0.034			34	9.4	1.3
	C-A				8.0				1.6
CCS observed*		0.43	0.41	1.30	19	24	25	8.0	1.8
CCS expected†		0.40	0.43	1.29	19.0	27.8	26.0	8.6	1.73

* Copenhagen Standard Seawater.
† From Riley and Chester (1971).

chamber. Standards containing 5 to 50 mg Cl/L were prepared from a 1000-mg Cl/L stock solution of "Specpure" NaCl (Johnson, Mathey and Co., Ltd.). Samples were diluted 10 to 1000 times to bring their Cl concentrations into the working range of the standards.

Precision of all of the above chemical analysis methods was ±10% or better.

Seawater analysis

As an additional verification of the accuracy of the analytical methods used, a sample of Copenhagen Standard Seawater (CSS) was diluted appropriately and analyzed along with the brine samples. Measured concentrations, included in Tables 2 and 3, conform very closely to the expected values.

RESULTS AND DISCUSSION

Core locations

Figure 2 presents a cross section of the McMurdo Ice Shelf in the area of interest. It shows the location of drill holes that penetrated brine, together

with the brine layer and shelf bottom as determined by drilling and radar profilometry (Kovacs and Gow 1977, Kovacs et al. 1982a, b). Two cores were drilled during the 1976–77 austral summer on either side of a prominent 4.4-m-high brine step (Fig. 3): the 77 High Step and the 77 Low Step cores. During the 1978–79 austral summer, five more cores were drilled at locations A, B, C, D and E. Figure 2 is drawn for the brine layer as it existed in January 1977. Observations made during the second field season (November 1978) showed that the brine step had further infiltrated the ice shelf and that it was now located at position C, a net inland movement of 700 m in a little less than 2 years (Kovacs et al. 1982b).

Preliminary observations

This discovery of a migrating brine step demonstrated for the first time the dynamic wave-like nature of brine infiltration in the McMurdo Ice Shelf. According to this perception of events, the 77 High Step core penetrated the leading edge or nose of a brine wave riding on top of an older brine layer from which the 77 Low Step cores were obtained just a few metres beyond the 77 High
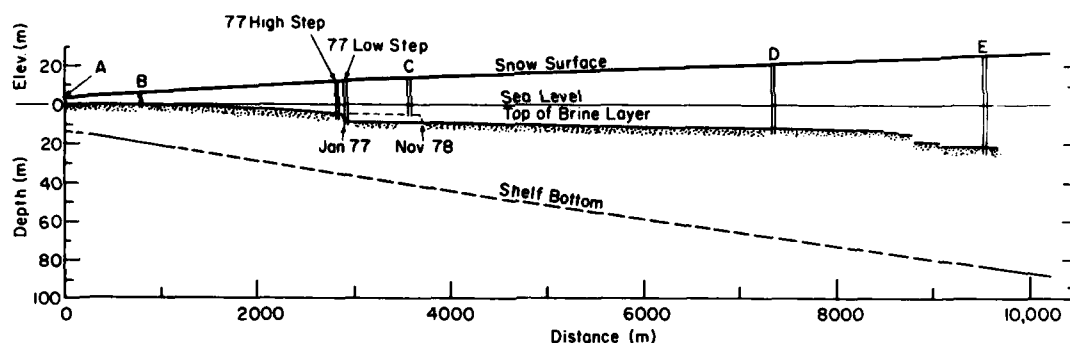

Figure 2. Cross section of McMurdo Ice Shelf showing top of brine zone and core drilling locations. The 10 January 1977 and the 24 November 1978 positions of the 4.4-m brine step and a series of steps near the inland boundary of brine penetration are also shown.
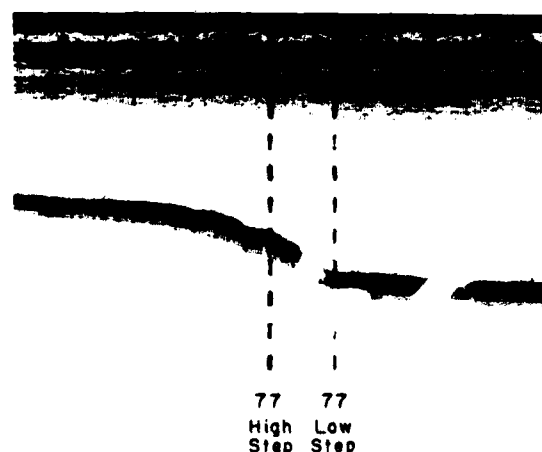

Figure 3. Graphic record of radio echo data showing the 4.4-m-high brine step in the McMurdo Ice Shelf as it appeared in January 1977. Locations of the 77 High Step and 77 Low Step drill holes are also indicated. Distance between drill holes is approximately 60 m.

5

Step drill core. Preliminary chemical analyses conducted before the brine step was resurveyed in November 1978 showed that brines from the 77 Low Step core had appreciably lower SO₄/Na ratios than brines from the 77 High Step core. At that time we interpreted this as indicating the presence of two chemically distinct brine layers in the immediate vicinity of the brine step. Drilling at site C penetrated the high side of the brine step as it existed in November 1978, after having migrated inland an additional 700 m since January 1977.

Brine chemistry

Tables 2 and 3 present the complete data of chemical concentrations and ionic weight ratios for samples from all seven drill holes. It should be noted that sample salinities and elemental concentrations vary because the brine has been diluted with meltwater from the firn of the cores. This dilution results in all samples having salinities and concentrations very much less than those of seawater. The amount of dilution is different for each sample so chemical concentrations or simple salinities cannot be used directly to determine if any salts are selectively precipitated. However, because the dilution water is known to be derived from firn, which is chemically much purer than seawater, ratios of elemental concentrations are not affected by dilution and should reveal any chemical fractionation that has occurred. The purity of McMurdo Ice Shelf firn is shown by chemical analysis of four samples from above the brine

zone in the 77 High Step core where Na concentrations averaged 4.3 mg/L, which is approximately three orders of magnitude less than Na concentrations in the brine-soaked firn.

A plot of Na concentration versus salinity (Fig. 4) shows a linear relationship with a least squares slope of 0.299 ($r = 0.972$). This agrees well with the expected slope of 0.319 for unfractionated seawater. There is no discernible difference between the Na/salinity ratio of fractionated and unfractionated core samples. Most of the scatter at the high salinity end of the curve is caused by samples from the 77 Low Step and 77 High Step cores where, as will be discussed later, chemical fractionation of the brine was actively taking place.

In studies of chemical fractionation of seawater, NaCl is generally considered to be chemically conservative, and elemental ratios are usually calculated relative to Cl or Na (Duce et al. 1972). We used Na as the reference element simply because the analytical measurement was less time-consuming than that for Cl.

Sulfate is the primary ion of interest. When seawater freezes, one of the first major salts to separate is sodium sulfate decahydrate (mirabilite), $Na_2SO_4 \cdot 10H_2O$, which begins to precipitate at $-8.2\,°C$ after sufficient water has been removed as ice (Lewis and Thompson 1950, Nelson and Thompson 1954). Sodium chloride dihydrate ($NaCl \cdot 2H_2O$) then follows at $-22.9\,°C$ (Nelson and Thompson 1954) but in situ McMurdo Ice Shelf temperatures, typically -12 to $-16\,°C$ in
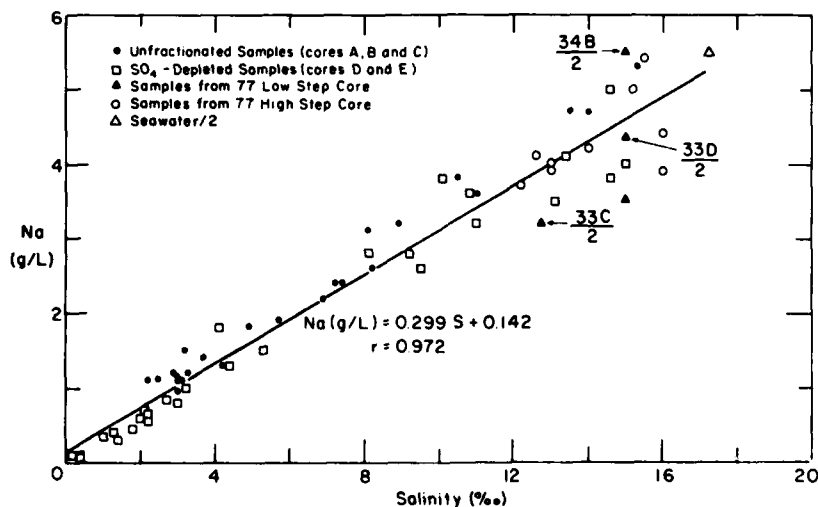

Figure 4. Variation in Na concentration with salinity in brine-soaked samples from the McMurdo Ice Shelf.

6

the deeper parts of the brine zone (Kovacs et al. 1982b), are not low enough to cause its precipitation.

The last column in Table 2 shows the reduction in SO_4/Na ratio for the brine from drill cores D and E; SO_4/Na ratios in the brine layer of this portion of the ice shelf are an order of magnitude lower than the normal seawater SO_4/Na ratio of 0.25. This lower ratio could be due to either a depletion of SO_4 or an enrichment of Na. To distinguish between these two mechanisms, we measured Cl concentrations in 14 samples of high and low salinities and from fractionated (low SO_4/Na ratio) and unfractionated (seawater SO_4/Na ratio) brines (see Table 3). The average Cl/Na ratio of 1.8 $\pm$0.3 is the same as the seawater Cl/Na ratio, indicating that Na is not enriched. Thus, the low SO_4/Na ratios observed in the brine from cores D and E must be due to depletion of SO_4.

The SO_4 depletion observed in the brine of drill cores D and E could result from precipitation of any of a number of alkali or alkaline earth salts of sulfate. The question is, which one? The least soluble of the SO_4 salts is $CaSO_4$ and Richardson (1976) reported the presence of $CaSO_4 \cdot 2H_2O$ in sea ice. But the average Na/Ca ratio (Table 3) of three SO_4-depleted brine samples is 26, which isn't appreciably higher than the seawater Na/Ca ratio of 25. Neither do changes in Ca concentrations parallel changes in SO_4 concentrations. Furthermore, there is not enough Ca in seawater to precipitate the amount of SO_4 that was removed. For example, in going from sample 5-B (core 77 High Step) to sample 33-C (core 77 Low Step) the SO_4 concentration drops by 2.0 g SO_4/L, from 2.5 g SO_4/L to 0.5 g SO_4/L. When salinities of these samples are corrected for dilution, the real concentration change is about 4.0 g SO_4/L. On a molar equivalent basis, 1.6 g Ca/L would be required to precipitate this amount of sulfate; this is almost four times the concentration of Ca (0.425 g Ca/L) in seawater. An additional calculation will further show that even if all the Ca in seawater (0.011 m/L) is removed as $CaSO_4$ then 0.018 m SO_4/L (1.73 g SO_4/L) would remain; the SO_4/Na ratio would then be 0.16, which is still six times greater than that observed for the fractionated samples. This means that some other cation is removing SO_4.

Some investigators have reported the precipitation of other insoluble Ca salts from seawater. Jones and Coote (1981) report that as seawater is frozen, the first salt to precipitate is $CaCO_3 \cdot 6H_2O$, which separates just below the freezing point of seawater and before $Na_2SO_4 \cdot 10H_2O$ precipitates.

Assur (1958) and Richardson (1976) report the presence of $CaCO_3 \cdot 6H_2O$, although it was determined indirectly. Nelson and Thompson (1954) do not report this salt but this may be due to their failure to observe the small amount of precipitate present. Concentration of seawater by evaporation can also yield gypsum, $CaSO_4 \cdot 2H_2O$, and possibly dolomite, $CaMg(CO_3)_2$ (Riley and Chester 1971). Although it is generally believed that cryohydrates of $MgCl_2$ do not precipitate from seawater brine until temperatures drop to $-36\,°C$ or lower, Assur (1958) has suggested and Richardson (1976) has confirmed that $MgCl_2 \cdot 8H_2O$ begins forming at about $-18\,°C$.

Even though seawater contains enough Mg to conceivably remove all of the SO_4, the good agreement between the seawater Na/Mg ratio and that of the samples (Table 3) indicates that Mg is not being removed. This may be due to the high solubility of $MgSO_4$. Neither does K appear to be affected, as shown by the Na/K ratios.

It is more likely that Na_2SO_4 would precipitate since it is less soluble than K_2SO_4 and since seawater contains a much higher concentration of Na than of K. In fact, seawater contains such a high concentration of Na that precipitation of all SO_4 as Na_2SO_4 would change the Na/K ratio by only 6% (from a normal 27.8 to 26.1). Thus, the high seawater concentration of Na permits the SO_4 to be removed as Na_2SO_4 without causing an appreciable change in the ratios of Na/K, Na/Mg or Na/Ca. Also, because of the small relative change in Na concentration when Na_2SO_4 precipitates, changes in the SO_4/Na ratio essentially reflect changes in the SO_4 concentration.

Sulfate is depleted as much as ten-fold in samples from cores E, D and 77 Low Step (Table 2). Cores E and D are the farthest inland from the ice front and correspond to the deepest and oldest brine layers (Fig. 2). Samples from the 77 Low Step cores are also from an older brine zone currently being overridden by a new wave of brine that was sampled first at 77 High Step and then approximately 22 months later at location C (see Fig. 2). Samples from these latter two cores together with brine samples from cores A and B show no significant SO_4 depletion and have essentially normal seawater SO_4/Na ratios; this is reasonable because cores A and B are located closest to the ice front and contain brine from the most recent intrusion of seawater.

Brine wave dynamics

As noted earlier the brine step at location C, as of 28 November 1978, is in reality the leading edge

7

of a brine wave migrating through the ice shelf in a direction opposite to the movement of the ice shelf itself. Because of glacial flow the McMurdo Ice Shelf is moving toward McMurdo Sound at rates of 47 to 118 m/yr (Heine 1968), depending upon location. At Heine's station 307, located very close to drill site E, the ice shelf is moving at a measured velocity of 84 m/yr. Drill site E is very close to the inland boundary of brine infiltration where the rate of migration of the deepest brine layer is only about 12 m/yr (Kovacs et al. 1982b). This means that in terms of its geographical location the brine terminus is currently moving seaward with the ice shelf at a velocity of about 72 m/yr.

Brine migration within the ice shelf is controlled by the permeability and temperature of the firn and ice and is maintained or renewed by seawater entering at the ice front. As demonstrated by Kovacs et al. (1982b) the overall process of infiltration is dominated by wave-like intrusions of seawater triggered by periodic break-out of the ice front in McMurdo Sound. (See cover for schematics of break-out.) The 4.4-m brine step, originally detected at the 77 High Step and 77 Low Step drill sites and which subsequently migrated to location C, represents the most recent example of a wave generated by a major break-out of the McMurdo Ice Shelf. This break-out is estimated to have taken place about 1970. Several other steps (waves) have been identified in radio echo profiling records by Kovacs et al. (1982b), including several very prominent steps near the terminal boundary of brine migration.

Infiltration of seawater into the McMurdo Ice Shelf is accompanied by freeze-concentration of the brine and freeze-fractionation of component salts, particularly mirabilite. The younger brine waves penetrate the ice shelf by simple permeation through porous firn. On 10 January 1977 the leading edge of the 4.4-m brine wave was located 2.85 km from the shelf edge and by 24 November 1978 it had migrated to a position 3.55 km from the ice shelf edge—an average rate of migration of 1.04 m/day. When the core at location C was drilled in November 1978 it penetrated the high side of the brine wave and SO$_4$/Na ratios were found to be close to that of unfractionated seawater.

When sufficient water (approximately 80%) is removed by freezing and the brine temperature reaches $-8.2°C$, mirabilite (Na$_2$SO$_4 \cdot$10H$_2$O) begins to precipitate out of solution (Nelson and Thompson 1954). Precipitation occurs at the leading edge of the brine wave where the salt concen-

tration is the highest and the temperature is lowest. The chemical fractionation is clearly demonstrated in samples from the 77 High Step and 77 Low Step cores. In samples from the 77 High Step core, SO$_4$/Na ratios vary from 0.5 to 0.68 (Table 2), which is about twice the normal seawater ratio of 0.25. This excess SO$_4$ in the 77 High Step samples can be attributed to inclusion of freshly precipitated mirabilite at the forward edge or nose of the brine wave. By contrast SO$_4$/Na ratios in samples from the 77 Low Step core located directly inland of the brine wave are much lower (2.3 to 4.5 times less) than that of normal seawater. The 77 Low Step cores are depleted in SO$_4$ because they were obtained from an older fractionated brine layer over which the new brine wave is migrating. The 77 High Step and 77 Low Step cores were taken within 60 m of each other so that the dramatic ten-fold change in SO$_4$/Na ratios occurs over a very short horizontal distance. As noted earlier it was this discontinuity in the brine chemistry on either side of the 4.4-m brine step that yielded the first clue of the dynamic structure of this step.

The deepest and oldest brine layer, sampled at drill site E near the inland boundary of brine penetration, contains highly concentrated brine in which the SO$_4$/Na ratio is an order of magnitude less than that of normal seawater (Table 2). Despite the fact that this brine is now enclosed within impermeable ice (Kovacs et al. 1982a), migration of the brine has not ceased. Movement on the order of 0.04 m/day has been measured (Kovacs et al. 1982b) and one possible explanation of this continued migration of brine is the eutectic dissolution of ice by the concentrated brine as it is transported into deeper and warmer parts of the ice shelf by the combined process of surface snow accumulation and bottom melting.

CONCLUSIONS

Chemical analyses of cores from a 4.4-m-high step in the brine-soaked firn of the McMurdo Ice Shelf confirm that this step is the leading edge of a brine wave that originated from seawater entering the ice front after a major break-out of shelf ice in McMurdo Sound around 1970. As the seawater begins to permeate the porous firn in the ice shelf, water is removed by freezing and concentrated brine begins to form. When the brine reaches a concentration of about five times that of the original seawater and a eutectic temperature of

8

−8.2°C, mirabilite ($Na_2SO_4 \cdot 10H_2O$) begins precipitating at the wave front. As the brine wave advances further inland, mirabilite continues to separate until the residual brine contains less than 10% of the original seawater SO_4. Once the brine has traveled far enough into the shelf to reach the firn–ice transition, further movement of the brine is slowed dramatically by impermeable ice. At this stage the salt concentration in the residual brine can be as much as seven times greater than that in the original seawater. The final salinity of this brine, now substantially depleted in SO_4, is determined by the in situ ice temperature, and we believe that the further slow migration is controlled by eutectic processes, including dissolution of ice by concentrated brine as it moves into deeper and warmer parts of the McMurdo Ice Shelf.

Thus, the overall brine zone consists of superimposed waves that originate at the shelf front during ice break-outs and migrate laterally at different velocities, depending on their position within the ice shelf. This wave-like migration through firn, in which brines become increasingly concentrated and dramatically depleted in sulfate, represents the principal mechanism by which seawater infiltrates the McMurdo Ice Shelf.

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